Chapter 11

In$_2$X$_3$ (X=S, Se, Te)
Semiconductor Thin Films: Fabrication, Properties, and Applications

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ABSTRACT

Indium chalcogenide thin film semiconductor compounds In$_2$X$_3$ (with X being a chalcogen atom, i.e., S, Se, or Te) are important materials in many current technological applications such as solar cells, micro-batteries, memory devices, etc. This chapter reviews the recent progress in In$_2$X$_3$ (X = S, Se, or Te) thin film research and development, with a particular attention paid to their growth and processing methods and parameters, and the effects that these have on the films microstructure. The intimate relationship between their fabrication conditions and the resulting physico-chemical and functional properties is discussed. Finally, results pertaining to the fabrication and characterization of these thin film materials, as well as the main devices and applications based on them are also highlighted and discussed in this chapter.

INTRODUCTION

Remarkable advances have taken place during the past few decades in semiconductor materials and devices. The semiconductor compounds of In$_2$X$_3$ family, where X is S, Se or Te have attracted particular interest in recent years due to their promising technological applications including a wide variety of devices. Among the important In$_2$X$_3$ devices that have been developed are solar cells (Yu et al, 1998), dry cells (Dalas & Kobotiatis, 1993), photochemical cells (Hara et al, 2000), solid state batteries (Julien et al, 1985), phase change memory devices (Lee & Kang, 2005; Lee & Kim, 2005; Hirohata et al, 2006), thin film strain gauge (Desai et al, 2005a), gas sensors (Desai, et al, 2005b), etc. Some In$_2$X$_3$ compounds can be used in Schottky diodes, capacitors, heterojunctions, and micro batteries (Kobbi, B., et al, 2001), and they also have a potential application as passivating layer for III-V semiconductor devices (Barron...
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1997. Many of the devices based on In2X3 have already found their way into industry.

A number of books, book chapters, and topical reviews are dedicated to semiconductor compounds such as II-VI, III-V and group IV (Adachi, 2005; Ahrenkiel, 1993; Chu & Chu, 1995; Shay & Wernick, 1975). However there is no review on In2X3 semiconductor compounds available in the literature. This article reviews the status of research on In2S3, In2Se3 and In2Te3 thin films, and focuses on their fabrication methods and functional properties. It also summarizes the recent advances in their relevant applications in many devices.

The interest in In2S3 thin films has increased during the last decade or so because of the high potential demonstrated by this material. With optimal physical properties, this material can meet the requirements for use as a window material or a buffer layer for photovoltaic device structures (Barreau et al, 2003). In2S3 can be used as an effective replacement for CdS in Cu(In,Ga)Se2 (CIGS) based solar cells (Spiering et al, 2003). Though the highest conversion efficiency in thin film solar cells has been reported for CIGS with CdS buffer layer, it is desirable to replace CdS with cadmium free buffer layers for environmental reasons (Hariskos et al, 2005; Naghavi et al, 2003a; Naghavi et al, 2003b; Sakata, 2000; Lee, et al, 2007).

Indium selenide (In2Se3) is another promising In2X3 material. In thin film form, it has valuable optical and electrical properties and is thus of interest for low-cost photovoltaic applications (Sahu, 1995; Lakshmikumar & Rastogi, 1994; Brahim-Otsmane et al, 1994; Hasehawa & Abe, 1982; Jayakrishnan et al, 2008). This is because of its high absorption coefficient as well as optimum energy band gap, suitable for solar energy conversion (Former et al, 1985; El-Sayed, 2004; Lee, et al, 2008; Bernede & Marsillac, 1997; Segure, et al, 1983; Qasrawi, 2007; Konagai et al, 1996). In2Se3 can also be used as a precursor for the growth of CuInSe2 absorber layer (Kim et al, 2005). The hexagonal layered structure of this material allows the change of the physical properties without destroying the initial structure. This characteristic makes it feasible to use this material in batteries (Balkanski, 1998; Julien, et al, 1989).

In2Te3 is also drawing attention due to its photoconducting properties (Guettari et al, 2003; Bose & De Purkayastha, 1981) and for its switching and memory effects (Balevicius et al, 1975; Balevicius et al, 1976; Afifi et al, 1996). The research and development of highly sensitive In2Te3 as gas detector and thin film screw gauge have attracted growing interest (Desai et al, 2005a; Afifi et al, 1995; Lakshminarayana et al, 2002; Hussein & Nagat, 1989).

FABRICATION PROCESSES

The properties of In2X3 thin films usually show a strong dependence on the film deposition technique and conditions as well as on the post-deposition heat treatment. The deposition method also has an impact on the overall fabrication cost.

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Deposition Methods

A wide range of methods exist for growing In2S3 thin films. In2S3 thin films are deposited using both wet and dry processes. Prominent among them are low pressure metal-organic chemical vapor deposition (MOCVD) (Horley et al, 1999), atomic layer chemical vapor deposition (ALCVD) (Spiering et al, 2003), spray pyrolysis (Jayakrishnan et al, 2005; Bhira et al, 2000; Pai et al, 2005), chemical bath deposition (CBD) (Barreau et al, 2002), atomic layer epitaxy (ALE) (Yousfi, et al, 2000a; Yousfi et al, 2000b; Asikainen et al, 1994), photochemical deposition (Kumaresan et al, 2002), annealing of elemental layers (Barreau et al, 2000a; Barreau et al, 2001), physical vapor deposition (PVD) (Barreau et al, 2002; Trigo
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